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(54) Title: GYPSUM PRODUCT

(57) Abstract

An aqueous emulsion comprising water and: (a) a petroleum-derived hydrocarbon wax; (b) a minor amount, by weight relative to (a) of montan wax; (c) a colloid stabilised emulsifier system which is used to increase the water resistance and/or improve the foaming of a gypsum product, for instance a lined board. The colloid stabilised system usually comprises a clay, for instance a montmorillonite clay. The emulsion is added to the gypsum slurry used in the manufacture of gypsum boards, tiles or blocks.

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GYPSUM PRODUCT

This invention relates to gypsum product and to a process for its manufacture. More particularly, this invention relates to gypsum product of improved water resistance and/or reduced density and to a process, preferably to a continuous process, for its manufacture.

Gypsum board (or plaster board or wallboard) is used extensively in the construction industry. It typically comprises a substantially flat core of set gypsum on either side of which a liner may be adhered. A liner typically comprises paper. The core may be reinforced; for example, reinforced with glass fibres.

Gypsum products (or Plaster of Paris or plast r products) are produced by mixing anhydrous calcium sulphate or calcium sulphate hemihydrate with water and permitting the mixture to set thereby producing calcium sulphate dihydrate. A pervasive problem with gypsum products, however, is that calcium sulphate dihydrate absorbs water and this reduces the strength of the gypsum product. Because of this, plaster board (for example) is required, at least in uses where a relatively high humidity is anticipated (for example, kitchens or bathrooms) to be substantially moisture resistant and this requires the presence of a hydrophobing agent. ("Hydrophobing" is a term used in the art to denote a method of preventing, or reducing water absorption).

Silicone oil has previously been used as a hydrophobing agent for gypsum products. It is, however, expensive and in relatively short supply. It also has difficulty in providing a moisture resistance of less than 5 wt % water absorption.

In US-A-5437722 an aqueous emulsion comprising a hydrocarbon wax, a montan wax and emulsifier/stabiliser system and also including a polyvinyl alcohol, is used to render gypsum products water resistant. The emulsifier system may include non-ionic or anionic surfactant and alkali.

This invention seeks to provide a gypsum product such as a gypsum board which has an improved water resistance.

In accordance with one aspect of the present invention, there is provided an aqueous emulsion which comprises water and:

(a) a petroleum - derived hydrocarbon wax;

(b) a minor amount by weight, relative to (a), of a montan wax;

(c) a colloid stabilised emulsifier system.

The aqueous emulsions of the present invention are found to have two distinct beneficial effects. First, they furnish the gypsum product with improved water resistance. Secondly, it is also found that they to facilitate production of low density gypsum product, especially gypsum board.

The petroleum - derived hydrocarbon wax (a) is preferably one with a high melting point and a low oil content. A preferred such wax is a paraffin wax, such as fully refined paraffin wax. Fully refined paraffin waxes are generally obtained from highly paraffinic refinery streams such as those obtained from the solvent dewaxing of distillates and other lube fractions. The product is further typically characterised as follows:

CHARACTERISTICS	TEST METHOD	SPECIFICATION	
		MIN	MAX
Congealing Point (°C)	ASTM D938	55	69
Oil in Wax (%)	ASTM D721		1
Penetration at 25°C (mm/10)	ASTM D1321	10	20
Penetration at 50°C (mm/10)	ASTM D1321		80
Viscosity (cSt @ 100°C)	ASTM D445	3	7

An xample of a fully refined paraffin wax which has been found to be entirely satisfactory, and which satisfies

the above specification, is MOBILWAX 135 (derived from the 150 SPN stream) as supplied by Mobil Oil Company Limited; MOBILWAX 145 or 150 (derived from the 300 or 450 SPN stream) are also suitable. While these waxes are hydrofinished to give a white colour and good odour, unfinished wax (which differs only in colour and odour) is also suitable for use in accordance with the invention. The petroleum - derived hydrocarbon wax a) suitably comprises from 20 to 40 wt % of the aqueous emulsion, preferably from 25 to 35 wt % of the aqueous emulsion.

The montan wax or lignite wax b) is another wax with a high melting point. It is preferably used in crude (or raw) form. Such a product is typically characterised as follows:

CHARACTERISTICS	TEST METHOD	SPECIFICATION		PREFERRED SPECIFICATION	
		MIN	MAX	MIN	MAX
Congealing Point (°C)	ASTM D938	67	80	75	80
Acid Value (mg KOH/g)	ASTM D1980	10	37	10	20
Saponification Value (mgKOH/g)	ASTM D1962	35	100	65	90
Ash Content (% wt)	ASTM D482		1		1.0
Density at 20°C (g/cm^3)	ASTM D1298	0.95	1.04	0.95	1.04
Viscosity (cSt at 90°C)	ASTM D445	20	400	150	400
Viscosity (cSt at 100°C)	ASTM D445	20	200	60	150

The montan wax b) suitably comprises from 10 to 20 wt % of the aqueous emulsion, preferably from 11 to 15 wt % of the aqueous emulsion.

It is found that the emulsifier system used in the pres nt invention should be a colloid stabilised system.

All anionic emulsifiers tested were found, in the downstream gypsum product forming process steps, to collapse the gypsum slurry foam resulting in an unacceptably high density for the product. Colloid stabilised systems are preferred. Preferred examples of colloid stabilised systems include inorganic particles. Clay/surfactant systems are particularly preferred. Suitable surfactants include aryl sulphonates such as sodium naphthalene sulphonates. The surfactant is preferably used in an amount in the range 2 to 5% by weight in the emulsion. Of the many colloidal clay systems, magnesium or sodium montmorillonite (for instance the product supplied as BENTONE EW by Rheox Limited) has been found to be very suitable. The clay is used in an amount in the range 0.1 to 0.8% by weight in the emulsion. Gum stabilised systems such as gum ghatti or xanthan gum may be used, but organic colloids are less preferred.

The emulsifier system (i.e. the total of two or more components of a multi-component system) is suitably present in an amount from 1 to 6 wt %, preferably 2 to 5 wt %, of the aqueous emulsion.

This invention also provides a gypsum composition settable by hydration to form a water-resistant gypsum product, which comprises a mixture, for instance a slurry in water, of 100 parts by weight of gypsum and from 1 to 10, preferably from 3 to 5 parts by weight of an emulsion as herein defined. The slurry may contain a foaming agent, especially where the product is to be a lined board. The slurry suitably contains 50-60 weight % gypsum and 40-50 weight % water, preferably about 55% gypsum. An accelerator is usually added, for instance a slurry mix from a previous batch. This invention also provides a water-resistant gypsum product which comprises a set such composition whilst the product may be an unlined board, the invention is particularly applicable to a product which comprises a core product of a set such composition

sandwiched between a pair of liners. Preferably, the gypsum product comprises gypsum which is foamed.

The invention further provides a process for the preparation of a water-resistant gypsum board product, which process comprises forming a mixture which is a slurry in water containing 100 parts by weight of gypsum and from 1 to 10 parts by weight of an emulsion according to the invention; forming a layer of the mixture in a mould means and drying the layer of gypsum mixture, while permitting hydration of the gypsum, for form a board product. Preferably the process is continuous. Preferably a foaming agent is mixed into the slurry before the mixture is applied to the mould means. The process may be for forming tiles or blocks or boards. Blocks may be formed in moulds from which they are removed when set. Tiles or boards may be formed by spreading a layer of the gypsum mixture on a first planar substrate, a second planar substrate is positioned over the layer to form an assembly, and the mixture is allowed to set in the assembly. A gasket may be provided between the planar substrates. Where the product is a lined board, the first and second planar substrates are constituted by liner, for instance paper, usually supported in a mould. Where the product is to be unlined, the planar substrates are removed when the product is set. Where the product is a block, it is usually removed from a mould before the mixture is completely set, but when it is hard enough to handle.

This invention includes the use of an aqueous emulsion of the invention to furnish a gypsum product with water resistance and the use of an aqueous emulsion of the invention to aid foaming of a gypsum slurry, for instance to reduce the density of the set foamed gypsum product.

The following Examples illustrate the invention.

EXAMPLE 1

First the wax phase was prepared by dissolving 12 wt % crude montan wax (Crude Montan Wax supplied by Schuemann Sabol GmbH) in 30.3 wt % of fully refined paraffin wax

(MOBILWAX 135 supplied by Mobil Oil Company Limited) at a suitable raised temperature. 2.3 wt % sodium naphthalene sulphonate (TAMOL NN 9104 supplied by BASF) was added to the aqueous phase and stirred for 20 minutes. 0.4 wt % magnesium montmorillonite (BENTONE supplied by Rheox Limited) was then added to the aqueous phase and stirred for 10 minutes. The temperature was lowered to 100°C and the wax phase was next added to the aqueous phase, with stirring to form a pre-emulsion which was next recycled through a homogeniser, with no impressed pressure, for one sixth of a pass. Gradually, the pressure was increased to a value in the range 12-14 MPa (1800 to 2000 p.s.i.) and the emulsion recycled for a further pass to form an aqueous emulsion in accordance with the invention.

The emulsion was then tested for its performance in the production of a gypsum product. A conventional foaming agent was mixed with a suitable quantity water to generate a foam mixture. A gypsum slurry mix was prepared by adding 2.38 wt % wax emulsion (according to the invention or comparative) to 39.17 wt % water along with predetermined amounts of a wetting agent, starch and an accelerator in a total amount of 0.38 weight %. To this 58.07 wt % gypsum was added with stirring. The pre-generated foam mix was next added to the gypsum slurry to form a foamed gypsum slurry. The slurry was poured into a paper lined mould of 300 x 300 x 12.5 mm dimension and a second sheet of paper placed on top to form a gypsum coupon which was then dried in three stages of successively lower temperatures and longer times to a constant weight. The density and 2 hour water absorption were then determined. The density was calculated by dividing the dry weight of the test specimen by the mould volume. The water absorption was determined by cutting a test specimen measuring 280 x 280 mm from the coupon and immersing this specimen in a water bath at 23°C covered with 25 to 35 mm of water for 2 hours. Its weight before and after immersion was measured and the percentage increase calculated.

The results, which include comparative tests, are shown in the following TABLE. In these tests density and 2 hr water absorption were measured and reported i) using different emulsifier systems and also ii) using two other high congealing point waxes either alone (in the case of Sasol) or blended with paraffin wax (in the case of Vesto wax). The results are reported on a percentage of a current commercial product (standardised at 100%) which is the Vesto wax/paraffin wax blend used with the colloid stabiliser.

It will be seen that none of the anionic or mixed anionic non-ionic emulsifier systems gave a satisfactory result: in all cases both the water absorption and the density were higher than those achieved with the current commercial product. Montan wax with either non-ionic or with colloid stabilised emulsifier systems, gave an improvement with both emulsifier systems, the improvement being greater in the case of the colloid stabilised system in respect of both water absorption and density.

		Emulsifier			
Wax Phase	Measurement (Relative to standard)	Anionic (Comparative)	Anionic/Non-Ionic (Comparative)	Non-Ionic (Comparative)	Colloid Stabilised (Invention)
Sasol (Fischer Tropsch Wax)	Water Absorption	203	193	123	N/A*
	Density	124	118	122	N/A
Montan (Lignite Wax)	Water Absorption	N/A	N/A	94	83
	Density	N/A	N/A	92	85
Vestowax (Synthetic)	Water Absorption	N/A	106	N/A	100
	Density	N/A	129	N/A	100

(*"N/A" means that it was not possible to produce a stable emulsion).

EXAMPLE 2

First the wax phase was prepared by dissolving 8 wt % crude montan wax (Romonta M3 supplied by Romonta GmbH) in 29.3 wt % of fully refined paraffin wax (Mobilwax 135 supplied by Mobil Oil Company Limited) at a suitable raised temperature. This wax phase was then used to form an emulsion using the same components for the aqueous phase and the same quantities as Example 1.

The emulsion was suitable for use as a hydrophobing agent for gypsum, in the production of gypsum products including lined and unlined boards, blocks and tiles.

The invention will now be further described by way of example, with reference to the accompanying drawing, in which:

Fig. 1 represents, in perspective a diagrammatic view of part of a lined gypsum board manufacturing process; and

Fig. 2 represents, in side elevation, a diagrammatic detail view of part of the lined gypsum board manufacturing process.

First, the aqueous phase is formed by mixing the aqueous emulsion together with other additives. These other additives comprise an accelerator (used in an amount of 0.2 to 0.8 st % of the aqueous phase) which was added to increase the rate of set of the gypsum; starch (used in an amount of 0.3 to 0.6 wt % of the aqueous phase) which was added to provide an adhesive to bond the plaster to the paper; and a wetting agent (used in an amount of 0.1 to 0.4 wt % of the aqueous phase) which was added to aid the dispersion of the aqueous phase with the dry gypsum plaster. This is then added to the gypsum plaster to form a plaster slurry.

A forming station for gypsum board manufacture is shown generally at 100. It comprises a conveyor 1 which is formed from an array of like, generally coplanar, parallel driven rollers 2 which are rotatable in the same sense. Above the conveyor is a manifold mixing box 3 into which

entry conduits 4 and 5 and a plurality of exit nozzles 6,6',6" are flowably connected. A contra-rotatable roller 7 is biased toward rollers 2 to form a nip 8.

In use, a plaster slurry 9 and the pre-generated foam mix 10, detailed above, are supplied under gravity, in an appropriate ratio, though conduits 4 and 5, respectively, into mixing box 3 where they are mixed to form a foamed plaster mixture 11. The foamed plaster mixture is then sprayed through the plurality of nozzles 6,6',6" onto a lower paper liner 12 which is being continuously conveyed, in the direction indicated, by rollers 2. The foamed plaster mixture becomes substantially evenly distributed across, and adheres to, the paper liner. An upper paper liner 13 is continuously conveyed, in the direction indicated by roller 7 into nip 8 where buildup of, the foamed plaster mixture into a dam 9 occurs and the plaster mixture adheres to the paper 13. Uncured plasterboard 14 is continuously conveyed downstream from the forming station along a long conveyor belt allowing the chemical reactions of setting to take place. It is then cut to th required length; and dried by passage through multideck drying zones.

In an alternative process, which is not illustrated, a non-foamed slurry is poured into block shaped moulds, in which it is allowed to set partially. The blocks are hard enough to handle after a few minutes, at which time they are pushed from the mould using, for instance, a hydraulic jack, and are conveyed to an oven to complete the setting/drying process.

CLAIMS

1. An aqueous emulsion which comprises water and:
   (a) a petroleum - derived hydrocarbon wax;
   (b) a minor amount, by weight relative to a) of montan wax;
   (c) a colloid stabilised emulsifier system.

2. An emulsion according to claim 1 wherein (a) comprises a paraffin wax.

3. An emulsion according to claim 1 or 2 wherein (a) comprises from 20 to 40 wt % of the aqueous emulsion.

4. An emulsion according to any preceding claim wherein (b) comprises from 10 to 20 wt % of the aqueous emulsion.

5. An emulsion according to any preceding claim wher in (c) comprises from 1 to 6 wt % of the aqueous emulsion.

6. A gypsum composition, settable by hydration to form a water-resistant gypsum product, which comprises a mixture of 100 parts by weight of gypsum and from 1 to 10 parts by weight of an emulsion according to any preceding claim.

7. A gypsum composition according to claim 6 which is a slurry comprising 60 to 100 parts of water.

8. A composition according to claim 6 or claim 7 comprising a foaming agent.

9. A water-resistant gypsum product which comprises a set composition of any of claims 6 to 8.

10. A water-resistant gypsum product which comprises a core product according to claim 9 sandwiched between a pair of adhered liners.

11. A water-resistant gypsum product according to claim 9 or 10 wherein the gypsum is foamed.

12. A process for the preparation of a water-resistant gypsum product, which process comprises forming a mixture which is a slurry in water comprising 100 parts by weight of gypsum and from 1 to 10 parts by weight of an emulsion according to any of claims 1 to 5; forming a layer of the mixture in a mould means; and drying the mixture while

permitting hydration of the gypsum, to form a set gypsum product.

13. A process according to claim 12 in which the mixture contains a foaming agent.

14. A process according to claim 12 or claim 13 in which the mould means comprises a first liner onto which the layer of mixture is applied and a second liner which is disposed over the layer to form an assembly of liners with the layer sandwiched therebetween, the assembly then being subjected to drying and hydration of said layer.

Fig.1.

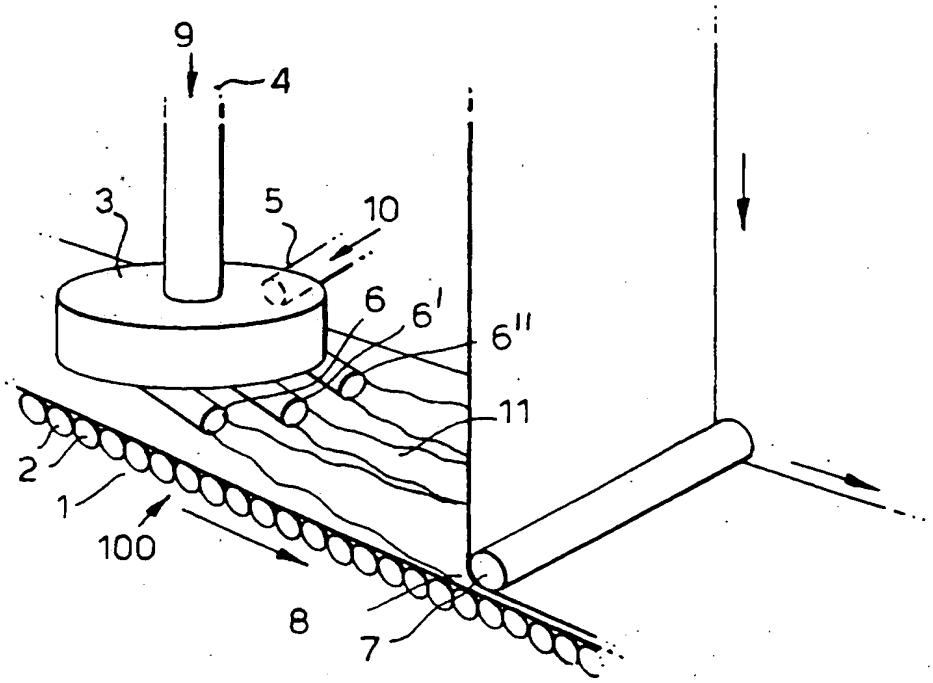
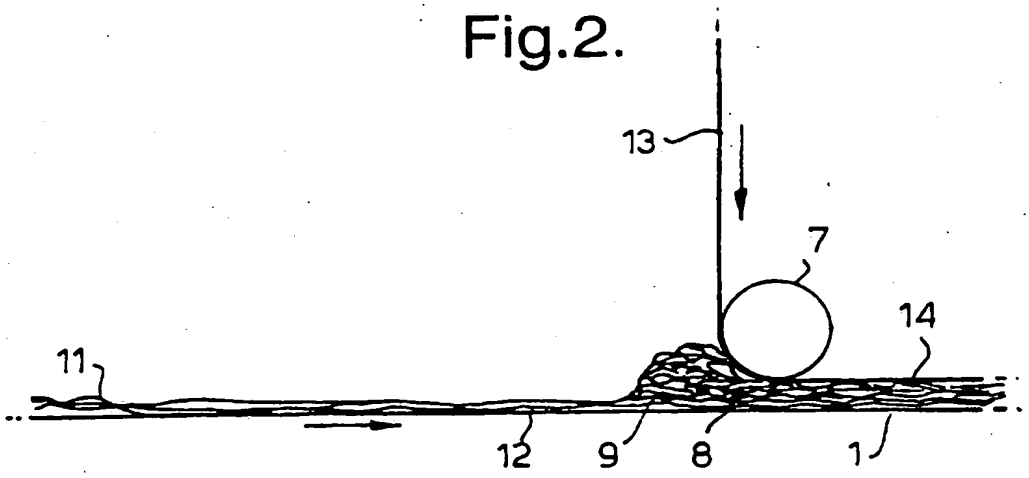


Fig.2.



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C04B28/14 C08L91/08 C08K3/34 //(C04B28/14,14:10,24:08, 24:36),(C08L91/08,91:06)

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US 2 031 171 A (H.K. LINZELL) 18 February 1936 see claim 4 ---	1-4,6, 8-14
A	FR 2 154 182 A (SHELL INT RES MIJ NV) 4 May 1973 see claims 1,2,4 ---	1
A	DE 211 877 C (J. KATHE) 13 July 1909 see page 1, line 28-30 ---	1
A	GB 2 223 235 A (ABSTER COMPANY LIMITED) 4 April 1990 see page 4, line 5-11; claims 1,3,12 ---	1
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[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category '	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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